Conformations of a Phenyl Group, and its Effect on the Barrier to Rotation in Substituted Ethanes

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Barriers to rotation about the central butane bond of 2,2-dimethyl-3-phenylbutanes are unexpectedly low. This is discussed in terms of the conformation about the phenyl–C_α and C_α–C_β bonds. The low barrier may be due to a ground state interaction between an *ortho*-hydrogen and the 1-methyl group of the butane. Other evidence of this interaction is adduced.

We have recently shown [1] that the barrier to rotation in the series of compounds (1) rises as the size of group R increases, as can be seen for the results for (1a—c). This is no more than a general trend since the concept of the size of a group of atoms such as an alkyl group is not well defined, although a methyl group is quite clearly intermediate in size between a hydrogen atom and a t-butyl group. We have also pointed out [2] some secondary effects on barriers in compounds like (1), which indicate the importance of considering interactions other than the direct 1,2 kind along the bond under consideration.

One further member of series (1) which we studied,[1] the phenyl compound (1d) has a barrier to rotation of 10·2 kcal mol^{-1}, 0·2 kcal mol^{-1} *less* than the corresponding methyl compound (1b). A similar contrast between a methyl and a phenyl compound has been reported by Bushweller and Anderson,[3] who found that the barrier in (2; R = Ph) is 0·2 kcal mol^{-1} less than in (2; R = Me), while that in (3; R = Ph) is 1·5—2·0 kcal mol^{-1} less than that expected [4,5] for (3; R = Me). These phenyl compounds have unusually low barriers in terms of the usual concept of the size of a phenyl group, the *A* value [6] which in this case is the free energy difference between axial and equatorial phenylcyclohexane. This is 3·0 kcal mol^{-1},[6] considerably higher than the *A* value of a methyl group, 1·7 kcal mol^{-1}.

We felt that an explanation of the relatively low barrier of (1d) might be found from an analysis of the conformations of the phenyl group, a relatively untouched problem.

The Parallel and Perpendicular Conformations.—On the basis of the chemical shift of the hydrogens α to the phenyl ring in toluene, ethylbenzene, and isopropylbenzene, Ouellette and his co-workers [7] concluded that the preferred conformations about the phenyl–carbon

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[1] J. E. Anderson and H. Pearson, *Chem. Comm.*, 1971, 871.

[2] J. E. Anderson and H. Pearson, *J.C.S. Chem. Comm.*, 1972, 908.

[3] C. H. Bushweller and W. G. Anderson, *Tetrahedron Letters*, 1972, 1811.

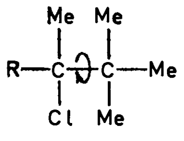
[4] J. E. Anderson and H. Pearson, *J. Amer. Chem. Soc.*, submitted for publication.

[5] C. H. Bushweller, W. J. Dewkett, J. W. O'Neil, and H. Beall, *J. Org. Chem.*, 1971, **36**, 3782.

[6] Original references for *A* values are quoted by J. A. Hirsch, *Topics Stereochem.*, 1967, **1**, 199.

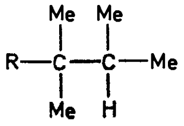
[7] R. J. Ouellette, B. K. Sinha, J. Stolfo, C. Levin, and S. Williams, *J. Amer. Chem. Soc.*, 1970, **92**, 7145.

bond in these latter two molecules have a hydrogen atom close to the plane of the ring as in (4; X = H or Me respectively), a *parallel* conformation. It might thus be a reasonable working hypothesis that in a trisubstituted toluene such as (5; L = large, M = medium, S = small) the preferred conformation is (6) with the small group in the plane of the ring.



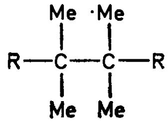
(1)

	R	$\Delta G^{\ddagger}$/kcal mol^{-1}
a;	H	8·3
b;	Me	10·4
c;	Bu^t	11·4
d;	Ph	10·2
e;	*o*-tolyl	



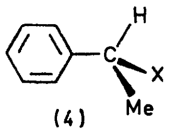
$R{-}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{C}}{-}\overset{\mathrm{Me}}{\underset{\mathrm{H}}{C}}{-}Me$

(2)

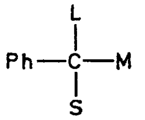


$R{-}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{C}}{-}\overset{\mathrm{Me}}{\underset{\mathrm{Me}}{C}}{-}R$

(3)



(4)



$Ph{-}\overset{\mathrm{L}}{\underset{\mathrm{S}}{C}}{-}M$

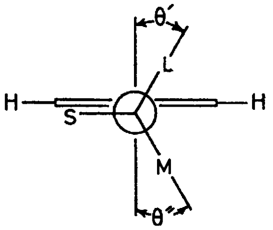
(5)

A different model conformation for such α,α,α-trisubstituted toluenes is provided by an enlightening study by the Allinger group [8] which comprises calculations of the conformational energy of the equatorial phenyl conformations of phenylcyclohexane (7) and 1-methyl-1-phenylcyclohexane (8). In phenylcyclohexane an α,α-disubstituted toluene, the benzylic hydrogen is concluded to be in the plane of the phenyl ring {*i.e.* as (6 with S = H, L,M = $[\mathrm{CH_2}]_5$)}, in agreement with the parallel conformation of Ouellette.[7] Introduction of a third α-substituent to give (8) however produces a change in conformation to a '*perpendicular*' [8] conformation shown in its generalised form as (9).

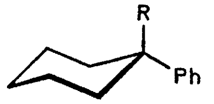
A structure such as (6) is in fact idealised, since we would expect (*a*) that mutual repulsion of the large and medium groups would reduce the angles θ' and θ'' below the ideal values of 30° shown,[9] and (*b*) that the group S is more likely to be *close* to the plane of the ring as in (10) depending on the interactions of the groups L and M. More generally, all symmetrical structures drawn here will be found to have, in fact, small distortions of bond angles and of dihedral angles to give lower energy conformations.* Nonetheless the concept of two limiting conformations, one, the parallel, where one rather small substituent is close to being in the plane of the phenyl ring and the second, the perpendicular, where the bond to the largest substituent is close to being orthogonal to the plane of the phenyl group, is a useful basis for discussion.

Since the perpendicular conformation has been postulated only for α,α,α-trisubstituted toluenes,† it is worthwhile asking how large substituents must be before this conformation is preferred. Information on three methyl substituents is provided by a crystal structure [10,11] of molecule (11). The t-butyl group with no *ortho*-substituents adopts a conformation much closer to a parallel one, with one methyl group at an angle of 9·5° to the plane, and the other two at 60 and 61° to the plane.[11]

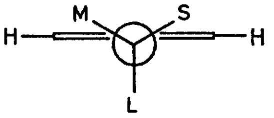
Although it may be dangerous to extrapolate results to the solution phase, these last results contradict Allinger's conclusions [8] and suggest that if one sub-



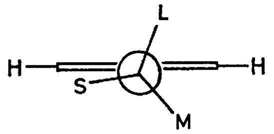
(6)



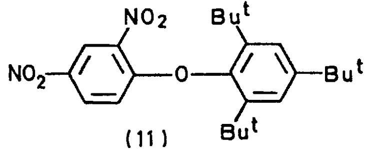
(7) R = H
(8) R = Me



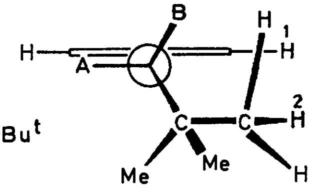
(9)



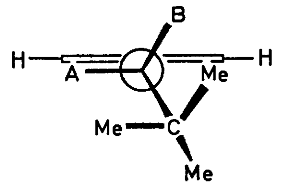
(10)



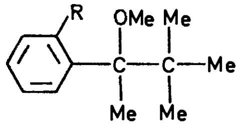
(11)



(12)



(13)



(14) R = H
(15) R = Me

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* Molecules may in fact be exchanging rapidly between two of these close-to-parallel conformations *via* the true parallel conformation if the molecule is symmetrical. Likewise with low-energy close-to-perpendicular conformations.

† We have postulated that in an extreme case, α,α-di-t-butyltoluenes both the large substituents will be close to perpendicular while at the same time the small substituent will be close to parallel.[9]

[8] N. L. Allinger and M. T. Tribble, *Tetrahedron Letters*, 1971, 3259.

[9] J. E. Anderson, H. Pearson, and D. I. Rawson, *J.C.S. Chem. Comm.*, 1973, 95.

[10] E. A. H. Griffith, W. D. Chandler, and B. E. Robertson, *Canad. J. Chem.*, 1972, **50**, 2963, 2972.

[11] B. E. Robertson, personal communication giving the angles quoted in this text.

stituent in a trisubstituted toluene is a methyl group or smaller, the preferred conformation will still be close to a parallel one as it is in simpler cases. It is with some consequences of this parallel conformation in molecules of type (1d) that this paper is concerned.

Having decided that the preferred conformation about the phenyl–C$_\alpha$ bond in (1d) is likely to be a parallel one, this can be either that one with the chlorine atom or the methyl group close to the plane of the phenyl ring. For convenience the discussion will be in terms of the conformation with the chlorine in the plane of the ring [*i.e.* (12; A = Cl, B = Me)] although the arguments which follow apply equally well to the other possibility, or to a rapidly interconverting equilibrium of the two.

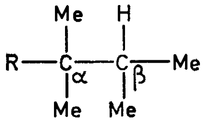
One bond further away from the phenyl group, the conformation about the C$_\alpha$–C$_\beta$ bond is presumably the symmetrically staggered one, and as (12) emphasises, there is as a consequence a strong interaction between one of the methyl groups of the t-butyl group and the *o*-hydrogen of the phenyl ring. If rotation about the C$_\alpha$–C$_\beta$ bond takes place, then eventually the eclipsed form (13) is reached, and in this conformation the interaction with the *o*-hydrogen of the phenyl group is reduced. It seems that herein might lie the explanation of the unexpectedly low barrier to rotation of the t-butyl group in (1d).

We tested this possibility in three ways. First we sought to prepare an *ortho*-substituted phenyl derivative (1e) with a view to measuring the barrier to rotation of the t-butyl group in that compound. The conformation about the phenyl–C$_\alpha$ bond should still be parallel, with the in-plane substituent (Me or Cl) directed away from the *ortho*-substituent. As a result, the interactions experienced by the methyl of the t-butyl group in its ground state conformation [(12) with H^1 replaced by Me] should be greater, as should be the relief of this interaction during rotation of the t-butyl group. Thus the barrier to rotation of the t-butyl group in (1e) should be even smaller than that of (1d), even though the substituent R is sterically larger.

In fact we were unable to synthesise (1e), all attempts to substitute the corresponding alcohol with a chlorine atom leading to elimination. We therefore prepared compounds (14) and (15), analogues of (1d and e) with the chlorine atom replaced by a methoxy-group. Measurement of the barrier to t-butyl group rotation in these compounds gave values of 9·4 and 7·7 kcal mol^{-1} respectively, precisely the effect expected on the basis of the long-range interaction discussed above. Thus introduction of the *o*-methyl substituent leads to a barrier to t-butyl rotation lower by 1·7 kcal mol^{-1}.

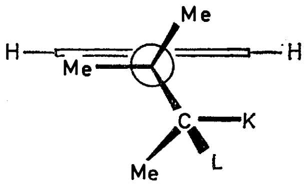
The spectrum of (15) shows, in addition, changes in the spectrum of all other signals. As the temperature is lowered from room temperature the aromatic methyl, *O*-methyl, and *C*-methyl signals, all singlets, broaden and appear below *ca.* 20° as unequal doublets of intensity ratio 1·97 : 1 at 11·4°, the less intense part being upfield in the case of the *C*-methyl signal, and downfield for the other two signals. The changes in the aromatic signal are complex, while in this temperature range the t-butyl signal is unchanged. The free energy difference between the species giving rise to these unequal spectra is 380 cal mol^{-1} at 11·4°. The spectrum of (14) shows changes in the complex spectrum of the aromatic hydrogens as the temperature is lowered below *ca.* −60°. These additional changes in the spectrum of (14) and (15) are analogous to changes in the spectrum of the aromatic hydrogens of compounds similar to (1d) which have been reported elsewhere,[9] and can be attributed to the slowing of rotation about the phenyl–C$_\alpha$ bond on the n.m.r. timescale. This will not be further analysed here.

As a second test of this hypothesis, we prepared compound (16a) which is similar to series (1), the important difference being that the three methyl substituents on the β-carbon atom (to give a t-butyl group) have been replaced by two methyl substituents and a hydrogen atom. The conformation about the C$_\alpha$–C$_\beta$ bond may have the phenyl and hydrogen substituents

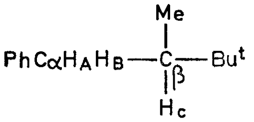


$R{-}C_\alpha(Me)_2{-}C_\beta H(Me){-}Me$

(16) a; R = Ph
b; R = Cl
c; R = Br
d; R = I

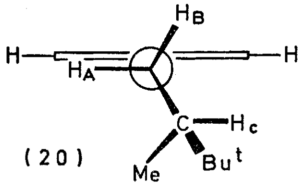


(17) K = H, L = Me *gauche*
(18) K = Me, L = H *trans*

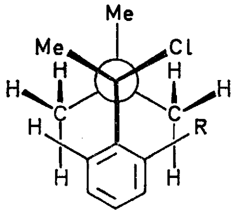


$PhC_\alpha H_AH_B{-}C_\beta(Me)(H_c){-}Bu^t$

(19)



(20)



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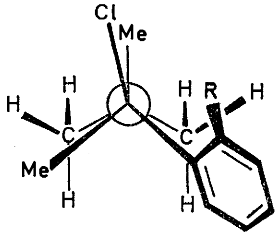

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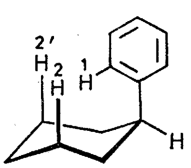

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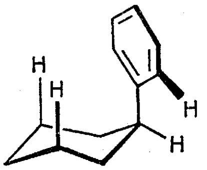

(24)

either *gauche* or *trans*. The destabilising methyl–*ortho*-hydrogen interaction found in (1d) is removed in the *gauche*-conformation (17) but it is still present in the *trans*-conformation (18). We thus expected that for (16a) the *gauche*-conformation would predominate, even though for analogous compounds with a halogen atom instead of the phenyl group (16b—d) the *trans*-conformation is more stable than the *gauche* by 0·28—0·75 kcal mol^{-1}.[12]

As the temperature is lowered, the spectrum of (16a) changes, the singlet for the two methyl groups nearest the benzene ring changing to a doublet and the doublet for the isopropyl group splitting to two doublets. There is no sign of further signals for these groups although we would probably not be able to distinguish $<5\%$ of a minor isomer. The nature of the spectral changes indicates that the *gauche*-conformation is present to $>95\%$ at low temperatures, the *trans*-conformation being particularly unstable. The changes as the temperature rises to room temperature are due to rapid interconversion of enantiomeric *gauche*-conformations. This contrast with the results quoted above for (16b—d) can reasonably be taken as further evidence for the importance of interactions with the *ortho*-position by a β-methyl group. The predominance of the *gauche*-conformation has also been recorded, without comment by Bushweller and Anderson.[3]

As a third test of the hypothesis, we considered the compound 2,3,3-trimethyl-1-phenylbutane (19). The hypothesis suggests that (*a*) the conformation about the phenyl-C_α bond is parallel and that as far as the C_α–C_β bond is concerned, (*b*) the small hydrogen atom H_c is nearest the *ortho*-hydrogen, and (*c*) the t-butyl group is *trans* to the phenyl group. If this is true then there is only one conformation, *viz*. (20), that the molecule can adopt.* In (20) H_A and H_B which are diastereotopic due to the asymmetry of the β-carbon atom are in addition very different in their relationship to H_C, and this should be reflected in the coupling patterns.

The spectrum of (19) bears out these expectations, for one hydrogen appears at δ 2·04 and the other at δ 3·00 and they are mutually coupled with ^2J 12·9 Hz. The former is coupled to H_C with ^3J 11·2 Hz while the latter is coupled to H_C with ^3J 2·5 Hz, and to the methyl group on C_β with ^4J 0·65 Hz. The large ^3J coupling of H_C to the hydrogen at δ 2·04 suggests that these atoms are *trans* to each other and that the signal at δ 2·04 be assigned to H_A of (20), and that at δ 3·00 to H_B of (20). The small ^3J coupling of H_B fits with the proposed *gauche*-arrangement of H_B and H_C, and the ^4J coupling to the methyl group on C_β further fits with H_B and with methyl group being *trans*, again as in (20). The chemical shifts of H_A and H_B are quite distinct but the relative importance of the shielding effects of the phenyl group, and the three substituents on C_β is difficult to predict.

It cannot be said whether the coupling constants ^3J recorded for (19) represent pure *trans*- or pure *gauche*-arrangements, but so large is the difference that the conformation of (19) must be almost 100% of one form as far as the conformation about the C_α–C_β bond is concerned and this form is shown in (20). In so far as (20) was predicted by the hypotheses on the conformation about the phenyl–C_α bond, and the interaction with an *ortho*-substituent, these hypotheses are strengthened.

The arguments presented above depend very much on the assumption of a parallel conformation, the justification for which though strong is by no means conclusive. It is worth considering the conformational situation if the preferred conformations of (1d and e) are perpendicular, or if that of (1e) is perpendicular as a consequence of the introduction of the *ortho*-substituent. The ground state and transition state conformations for t-butyl rotation are best considered in the forms (21) and (22). (22) Is that conformation in which the phenyl group presents its face directly to the eclipsing methyl group which lies directly above the axis of symmetry of the phenyl group. When R = H it has no obviously strong interaction in either form, but when R = Me, there is an interaction with one methyl of the t-butyl group in the ground state (21) which is reduced in going to the transition state (22). This consideration of these molecules in terms of only the perpendicular conformation does explain the lower barrier in the *ortho*-substituted case (15) but not what we claim to be an unusually low barrier in compounds (1d) and (14). Equally it does not explain the preference for the *gauche*-conformation in compound (16a).

This work indicates then a further secondary steric effect on rotation in highly substituted ethanes. If the principal torsional interaction along an ethane bond be labelled α or 1,2, the interaction of H^1 and H^2 in (12) which we have shown to have some conformational consequences is a δ or 1,5-interaction.

The particular hydrogen interaction involved in this effect [that of H^1 and H^2 shown in (12)] plays another important role in conformational analysis. The axial conformation of phenylcyclohexane should have the parallel conformation (23) as far as the conformation about the phenyl–carbon bond is concerned. In this conformation, however, the interaction of H^1 and H^2 or $H^{2'}$ is exactly analogous to that of H^1 and H^2 in (12), and in this probably lies the explanation of the particularly high *A* value of the phenyl group.[6,8] In fact calculations suggest [8] that in the axial phenyl conformation of phenylcyclohexane such interactions are so great that in this case a perpendicular conformation (24) is preferred.

As to the conformation about the phenyl–C_α bond, discussion in terms of a parallel conformation allows a rationalisation of all the results presented, whereas the perpendicular conformation does not seem to do so. Compared with the axial–equatorial equilibrium in

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* Thus a conformation like (20) but with H_B in the plane of the ring and H_C parallel as before would have the t-butyl group *gauche* to the phenyl ring.

[12] J. E. Anderson and H. Pearson, *J. Chem. Soc. Perkin II* 1973, 960; C. Doecke, unpublished results.

cyclohexanes, or the *gauche–trans*-equilibrium in substituted ethanes, the rotational equilibrium about the phenyl–C_α bond in substituted toluenes may never be well understood. This happens because the various conformations may not lie in energy terms at the foot of deep potential wells, which is a reflection of the almost zero barrier to rotation in toluene itself.[13] The application of n.m.r. to the study of this problem is handicapped by the lack of coupling between nuclei at opposite ends of the bond which might show angular dependence. As a result, knowledge has to be built up by indirect studies such as the present one, in which usually, conclusions can only be suggested, not proven.

EXPERIMENTAL

N.m.r. spectra were recorded as described previously.[1,14]

3,3-Dimethyl-2-phenylbutan-2-ol.—A 70 : 30 benzene–ether solution of phenyl-lithium (50 ml, 50 mmol) was slowly added, under nitrogen, to pinacolone (5 g, 50 mmol) in ether (25 ml) at room temperature. The contents of the flask refluxed gently during the addition. The solution was stirred for 1 h, then poured onto cracked ice (*ca.* 50 g), and the mixture was extracted with ether (30 ml). The ether extract was washed with water, dried ($MgSO_4$), and the solvent was removed at water-pump pressure to leave crude product (10·36 g). Distillation yielded the alcohol (*ca.* 6 g, 67%) as a clear liquid, b.p. 112—120° at 15 mmHg (lit.,[15] 95·5° at 4·5 mmHg), $\nu_{max.}$ 3490 cm^{-1} (OH), δ (CCl_4, 60 MHz), 0·90 (9H, s), 1·27 (1H, s), 1·55 (3H, s), and *ca.* 7·3 (5H, m).

3-Chloro-2,2-dimethyl-3-phenylbutane (1d).—Thionyl chloride (3·5 ml) was slowly added to the above alcohol (3·1 g, 17·4 mmol) at 0°. After standing overnight the mixture was poured onto cracked ice (*ca.* 10 g), extracted with ether (20 ml), the extract was washed with water (15 ml) and 5% sodium carbonate (15 ml), and dried ($MgSO_4$). The solvent was removed at water-pump pressure to leave the crude product which was distilled to yield the pure chloride (2·25 g, 68%) as a liquid, b.p. 64° at 0·2 mmHg (lit.,[15] 65° at 0·5 mmHg), n.m.r., see below.

3-Methoxy-2,2-dimethyl-3-phenylbutane (14).—3,3-Dimethyl-2-phenylbutan-2-ol (13·4 g, 61 mmol) in dimethyl sulphoxide (35 ml) was added to a stirred solution of sodium hydride (4 g, 166 mmol) in the same solvent (120 ml) and left overnight. Methyl iodide (11·4 g, 80 mmol) in the same solvent (15 ml) was added and stirring was continued overnight. Pentane (100 ml) and water (125 ml) were added. The *product* was extracted with ether, washed, dried, and distilled, b.p. 100—102° at 4 mmHg (Found: C, 81·6; H, 10·65. $C_{13}H_{20}O$ reqiires C, 81·2; H, 10·8%), n.m.r., see below.

3,3-Dimethyl-2-(o-tolyl)-butan-2-ol.—n-Butyl-lithium (15·2 ml of 2·0M solution) was added at 10° to *o*-bromotoluene (5 g, 29 mmol) in diethyl ether (40 ml). The solution was stirred for 1 h and then pinacolone (3·0 g, 30 mmol) was added. After a further 90 min stirring water (30 ml) was added. The ether layer was separated and dried and the ether removed. Distillation yielded the alcohol, b.p. 83° at 0·8 mmHg, identified from its n.m.r. spectrum, δ (CCl_4, 60 MHz) 0·95 (9H, s), 1·30 (1H, s), 1·63 (3H, s), 2·57 (3H, s), and *ca.* 7·0 (4H, m), but not characterised further.

3-Methoxy-2,2-dimethyl-3-(o-tolyl)butane (15).—This was prepared as for (14) and had b.p. 259—262° at 760 mmHg, n_D^{20} 1·4516 (Found: C, 81·25; H, 10·65. $C_{14}H_{22}O$ requires C, 81·5; H, 10·65%), n.m.r., see below.

2,3-Dimethyl-3-phenylbutane (16a).—This was prepared by hydrogenation of 2,3-dimethyl-3-phenylbut-1-ene and had b.p. 211° (lit.,[16] 210°).

2,3,3-Trimethyl-1-phenylbutane (19).—1-Phenyl-2,3,3-trimethylbutan-2-ol[14] (2 g, 10·4 mmol) and toluene-*p*-sulphonic acid (*ca.* 0·1 g) were distilled to give a mixture of olefins. Hydrogenation over 10% palladium on charcoal, followed by filtration and distillation yielded the *product* (19), b.p. 63° at 3 mmHg (Found: C, 88·25; H, 11·2. $C_{13}H_{20}$ requires C, 88·55; H, 11·45%), δ (CF_2Cl_2) 0·99 (9H, s), 0·76 (3H, dd, ^3J 6·7, ^4J 0·65 Hz), *ca.* 1·50 (1H, m), 2·52 [2H, m (see text)], and 7·11 (5H, m).

N.m.r. Spectra.—For (1d), at ambient probe temperature, the t-butyl signal appears as a singlet at δ 1·05, the β-Me group as a singlet at 2·02, and the phenyl signal is a complex multiplet between 7·09 and 7·62. At −107·1°, the t-butyl signal comprises three singlets at δ 1·29, 1·05, and 0·83. Temperatures and rate constants for t-butyl rotation are −84·7°, 5·0 s^{-1}; −80·2, 8·5; −77·1, 14·7; −76·1, 15·5; −75·0, 21; −72·9, 28; −70·9, 40·0; −68·8, 59; −66·7, 71; −64·6, 93; −62·8, 115; −60·9, 146; −60·4, 139; −58·1, 201; −55·0, 282; −51·8, 366; −50·2, 456; −47·8, 574. A plot of log k/T against $1/T$ gives $\Delta H^\ddagger$ 10·71 kcal mol^{-1}, $\Delta S^\ddagger$ 2·4 cal K^{-1} mol^{-1}.

For (14) the t-butyl signal appears as a singlet at δ 0·88 at ambient temperature, and as three lines at δ 1·08, 0·80, and 0·74 at −117·1°. Temperatures and rate constants for t-butyl rotation are −101·6°, 6·6 s^{-1}; −100·0, 8·4; −98·0, 10·7; −96·9, 14·1; −95·2, 20·3; −93·8, 21·9; −91·8, 25·7; −89·7, 42; −84·4, 57; −83·4, 75; −78·6, 121; −74·8, 226; −72·2, 300; −68·4, 460. A plot of log k/T against $1/T$ gives $\Delta H^\ddagger$ 8·33 kcal mol^{-1}, $\Delta S^\ddagger$ −5·1 cal K^{-1} mol^{-1}.

For (15) at ambient probe temperature, the t-butyl signal appears as a singlet at δ 0·93, β-Me as a singlet at 1·64, OMe as a singlet at 3·10, ArMe as a singlet at 2·56, and the aromatic hydrogens as a complex multiplet at *ca.* 7·2. Temperatures and rate constants for t-butyl rotation are −128·9°, 10 s^{-1}; −125·6, 17; −117·2, 50; −115·3, 68; −113·7, 90; −110·7, 123. A plot of log k/T against $1/T$ gives $\Delta H^\ddagger$ 6·11 kcal mol^{-1}, $\Delta S^\ddagger$ −10·2 cal K^{-1} mol^{-1}.

For (16a) at ambient probe temperature α-methyls appear as a singlet at δ 1·26, the β-methyls as a doublet (*J* 6·8 Hz) at 0·78, and the tertiary hydrogen appears as a septet (*J* 6·8 Hz) at 1·94. At *ca.* −125°, the α-methyls appear as equal singlets at δ 1·22 and 1·27, the β-methyls appear as two equal doublets at 0·51 and 1·06, and the tertiary hydrogen as a broad multiplet at 1·94. At all temperatures the aromatic hydrogens appear as a multiplet at δ 7·22.

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